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(54) [Title] **GAS BARRIER TYPE LOW MOISTURE PERMEABLE INSULATING TRANSPARENT SUBSTRATE FOR ELECTRODE AND ITS USE**

(57) [Abstract]
[CONSTITUTION] At least one layer of nitride transparent thin film and at least one layer of oxide transparent thin film are laminated on at least one surface of a transparent substrate, which comprises polyethersulfone or polyarylate. A macromolecule layer, for example a polyvinylalcohol etc., is laminated on this laminated body properly.
[EFFECT] To provide a gas barrier type low moisture premeable insulating transparent substrate for an electrode and a moisture-proof film for EL elements, which is suitable for the application to a liquid crystal display device that must avoid water vapor or oxygen.

[Claim(s)]

[Claim 1] A gas barrier low moisture permeable insulating transparent substrate for an electrode characterized by laminating of at least a single layer of transparent thin film which consists of nitride and at least a single layer of transparent thin film which consists of oxide transparent thin film on at least one of the surface of a transparent substrate.

[Claim 2] A gas barrier low moisture permeable insulating transparent substrate for an electrode according to Claim 1, wherein said transparent thin film comprising nitride is a monolayer transparent thin film or a multilayer transparent thin film, which consists of at least one sort in silicon nitride, indium nitride, gallium nitride, aluminum nitride, tin nitride, boron nitride, and chromium nitride.

[Claim 3] A gas barrier low moisture permeable insulating transparent substrate for an electrode according to Claim 1 or 2, wherein said transparent thin film comprising nitride consists of an oxidized material partly.

[Claim 4] A gas barrier low moisture permeable insulating transparent substrate for an electrode according to Claim 1 or 2, wherein said transparent thin film comprising nitride consists of a hydrogenated material partly.

[Claim 5] A gas barrier low moisture permeable insulating transparent substrate for an electrode according to Claim 1, wherein said transparent thin film comprising oxide is a monolayer transparent thin film or a multilayer transparent thin film, which consists of at least one sort in indium oxide, indium oxide・tin (ITO), tin oxide, zinc oxide, aluminum oxide, silicon oxide, titanium oxide, zirconium oxide, tantalum oxide, niobium oxide, and selenium oxide.

[Claim 6] A gas barrier low moisture permeable insulating transparent substrate for an electrode according to Claim 1, wherein a transparent macromolecule layer is laminated on said transparent substrate and/or on said transparent thin film.

[Claim 7] A gas barrier low moisture permeable insulating transparent substrate for an electrode according to Claim 1, wherein a transparent macromolecule layer is laminated on a transparent thin film of said transparent substrate for an electrode, further said transparent thin film, said transparent substrate are successively laminated.

[Claim 8] A gas barrier low moisture permeable insulating transparent substrate for an electrode according to Claim 7, wherein a hardening resin and/or the thermoplastic resin is laminated on at least one of the surface of said transparent substrate for an electrode.

[Claim 9] A gas barrier low moisture permeable insulating transparent substrate for an electrode according to Claim 6 or 7, wherein said transparent macromolecule layer consists of at least one sort in a gas-permeability-proof resin, an anchor-coat agent, a hardening resin, and thermoplastic resin.

[Claim 10] A gas barrier low moisture permeable insulating transparent substrate for an

electrode according to Claim 9, wherein said gas-permeability-proof resin is the polymer or the mixture containing at least one component at more than 60 mol % of cellulose component, polyamide system resinous principle, vinyl alcohol component, halogenation vinylidene component, acrylonitrile component, and amorphous polyester component.

[Claim 11] A gas barrier low moisture permeable insulating transparent substrate for an electrode according to Claim 9, wherein said anchor-coat agent consists of at least one sort of polyurethane, polyamide, polyethyleneimine, amorphous polyester, hydrophilic-property polyester, ion macromolecule complex, and alkyl titanate resin, those copolymers, or mixture.

[Claim 12] A gas barrier low moisture permeable insulating transparent substrate for an electrode according to Claim 9, wherein pre-hardening resin consists of at least one sort of urethane resin, epoxy resin, acrylic resin, acrylic-ester resin, phenoxy ether system, melamine resin, phenol resin, silicone resin, xylene resin, guanamine resin, diallyl phthalate resin, vinyl ester resin, polyimide, maleic resin, unsaturated polyester resin, and alkyd resin, those copolymers, or mixture.

[Claim 13] A gas barrier low moisture permeable insulating transparent substrate for an electrode according to Claim 9, wherein said thermoplastic resin consists of at least one sort of polypropylene, polyethylene, polyolefines such as ethylene propylene copolymer, polyester, polyamide, ionomer, ethylene-vinyl acetate copolymer, acrylic ester, acrylic resin such as methacrylic-acid ester, poly-vinyl acetal, phenol, denaturation epoxy resin, vinyl acetate resin, silicone RTV, polymer alloy type polyimides, these copolymers, or mixture.

[Claim 14] A gas barrier low moisture permeable transparent conductive electrode substrate characterized by forming a transparent conductive thin film on the at least one of the gas barrier low moisture permeable insulating transparent substrate for an electrode of Claim 1.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a gas barrier low moisture permeable transparent conductive substrate for an electrode and a gas barrier low moisture permeable transparent conductive electrode substrate formed by using them. In detail, this invention relates to an insulating transparent substrate for an electrode, which is excellent in the dampproofing which made the high polymer film the base material and in the gas barrier nature, and a gas barrier low moisture permeable transparent conductive electrode substrate formed by using them. Still in detail, this invention has the transparency in a visible region, and its permeability of gases such as oxygen and a

steam is small, and further relates to a transparent substrate for an electrode with the outstanding weatherability, the chemical-resistance and the abrasion resistance, that is to say, a gas barrier low moisture insulating transparent substrate for an electrode, which is suitable for the application to the liquid-crystal-display element that must avoid a steam, oxygen, in addition a detrimental gas, and an electroluminescence (electroluminescence devices, hereinafter called EL element) and so on, and a gas barrier low moisture permeable transparent conductive electrode substrate formed by using them.

[0002]

[Description of the Prior Art] Conventionally, although a glass has been used as a base material of a liquid crystal display transparent conductor, using a transparent conductive film for an electrode from the viewpoints 1) the formation of lightweight, 2) the formation of thinner films, 3) the formation of larger areas, 4) crash-proof nature, 5) the excellent workability, and 6) the diversification of configurations, is proposed in recent years. However, when a conductive film is used, it has turned out that steam and oxygen which penetrates a film cause the performance of degradation a liquid crystal device. In order to solve such a problem, it was necessary to give the barrier nature against a gas to the film base material.

[0003] For example, Japan Laid-Open Patent 59-204545 discloses a transparent conductive film, wherein an oxide layer is provided on a high polymer film and a film mainly contained indium oxide is formed on at least one side of these macromolecules layers. However, these oxides coat has imperfect steam barrier nature because of a fault such as that a crack tends to go into a thin film. If the vacuum evaporation of metals such as aluminum is performed, it cannot be used for a transparent electrode substrate since the steam barrier nature is exhibited but the transparency is spoiled remarkably.

[0004] Moreover, Japan Laid-Open Patent 63-205094 discloses a transparent conductive film, wherein an aluminum-nitride thin film is provided on a high polymer film and a transparent conductive film is formed on at least one side of these macromolecules layers. However, this aluminum-nitride thin film is a monolayer, and its gas barrier nature is inadequate, and it tends to harm, the aluminum nitride thin film is harmed at the time of the manipulation of the transparent conductivity having the aluminum-nitride thin film into a liquid crystal display element, a distributed EL element, etc., and the fall of the steam barrier nature of a transparent conductive film and gas barrier nature was seen. Moreover, the aluminum nitride had problems that it decomposed gradually to generate ammonia in a normal temperature when it suited water, or it generated to decompose ammonia when it suited acid, and had a further problem that the fall of the gas barrier nature after etching a conductive layer, etc. when

it applied to a liquid crystal display element, since the etching reagent of a conductive layer was acid.

[0005] The laminating of polyvinyl alcohol, an ethylene vinyl alcohol copolymer, three-fluoride monochloro ethylene, or the transparent metallic oxide to the high polymer film is proposed in Japan Laid-Open Patent 60-190342. Moreover, although the gas barrier nature film, which is laminated gas-permeability resins such as polymer containing more than 50 mol % of an acrylonitrile component or is laminated cross-linking resin hardened materials such as epoxy resin on a high polymer film provided the anchor-coat agent, is proposed in Japan Laid-Open Patent 63-71829. But the gas barrier nature film used only these organic substance layers for the high gas barrier layer abruptly falls in the air barrier nature under high humidity. That is, although the oxygen permeability in the pure oxygen status can hold a high level, the oxygen permeability in the status that a steam and oxygen were mixed falls remarkably.

[0006] Moreover, although mixing fluorine in a metallic-oxide layer in order to increase the electric insulation of the metallic oxide comprising In and Sn is proposed in Japan Laid-Open Patent 2-265738 as an enhancement of the moisture-proof film for EL elements whose oxide layer of the metal which consists of In and Sn was pinched by the high polymer film, the amount of fluorine must be controlled in order to increase the electric insulation of a metallic-oxide layer, and the adhesion with the metallic-oxide layer containing substrates and fluorine will become worse and it is possible to spoil the gas barrier nature if there are too many amounts of fluorine.

[0007] As mentioned above, in the case of preparing an independent layer of metallic oxide, it is difficult to remove every pinhole produced with the dirt of the particle in the equipment, a base film and the stress at the time of forming etc., and only independent layer of metallic oxide does not serve as sufficient barrier layer.

[0008] Moreover, although organic substance layers usually consist of resin of cellulose system, polyacrylonitrile system, polyvinylidene chloride system, polyamide system, etc., polyvinyl alcohol system resin, which has strong intermolecular force and high functional-group concentration, is desirable. However, since the polyvinyl alcohol system resin is hydrophilic, sufficient bond strength for direct adhesion to many high polymer films cannot be obtained in many cases, and under high humidity, water is absorbed, the compactness of structure is spoiled, and air barrier nature falls abruptly. Furthermore, since polyvinyl alcohol system resin is invaded by hydrochloric acid that is the etching reagent of a conductive layer, it cannot be used for the substrate for transparent electrodes for liquid crystal displays by polyvinyl alcohol system resin independently.

[0009] As mentioned above, in the conventional technique, there are some difficulty that steam barrier nature and gas barrier nature are not enough in maintaining

transparency, and transparency will be spoiled in holding more advanced steam barrier nature and gas barrier nature, and in holding transparency with at least one of steam barrier nature and gas barrier nature, the endurance is spoiled. Moreover, in fact in the environment where steam and oxygen near a reality and the status that it is used were mixed, oxygen permeability is high and there is a difficulty referred to as that oxygen permeability is influenced with the amount of steam.

[0010]

[Problem(s) to be Solved by the Invention] That is, the purpose of this invention is to offer a gas barrier low moisture permeable transparent conductive electrode substrate which comes to use an insulating transparent substrate for an electrode and this excellent in the gas barrier nature without the above troubles, and low moisture permeability.

[0011]

[Means for Solving the Problem] As a result of inquiring zealously to a resolution of such a problem, this inventor(s) has found that a pinhole with difficulty in an independent layer of nitride or oxide can be reduced by laminating for two layers, namely, by laminating oxide with gas permeability-proof and nitride with waterproof steamy permeability and laminating a transparent thin film with the waterproof steamy permeability, with few pinholes and with gas permeability-proof on a transparent substrate, and so that there is little influence on the oxygen permeability by the water vapor content and gas barrier nature and steam barrier nature also improve. Further, he has found out that by laminating a resin layer with gas permeability-proof, hardening resin and thermoplastic resin on them, the film is transparentand there is endurance which can also bear the physical impact and grinding at the time of the manipulation to a liquid crystal display element, an EL element, etc., moreover, it has the remarkably excellent steam barrier nature, the gas barrier nature, and the insulation, which oxygen permeability is hard to be influenced by the amount of a water vapor, and thus he reached this invention.

[0012] That is, this invention is a gas barrier low moisture permeable insulating transparent substrate for an electrode characterized by laminating of at least a single layer of transparent thin film which consists of nitride and at least a single layer of transparent thin film which consists of oxide transparent thin film on at least one of the surface of a transparent substrate.

[0013] As a desirable mode, this invention comprises:

a gas barrier low moisture permeable insulating transparent substrate for an electrode according to above-mentioned, wherein a transparent thin film comprising nitride is a monolayer transparent thin film or a multilayer transparent thin film, which consists of at least one sort in silicon nitride, indium nitride, gallium nitride, aluminum

nitride, tin nitride, boron nitride, and chromium nitride;

a gas barrier low moisture permeable insulating transparent substrate for an electrode, wherein a transparent thin film comprising nitride consists of an oxidized material partly; or

a gas barrier low moisture permeable insulating transparent substrate for an electrode, wherein a transparent thin film comprising nitride consists of a hydrogenated material partly; or

a gas barrier low moisture permeable insulating transparent substrate for an electrode, wherein a transparent thin film comprising oxide is a monolayer transparent thin film or a multilayer transparent thin film, which consists of at least one sort in indium oxide, indium oxide · tin (ITO), tin oxide, zinc oxide, aluminum oxide, silicon oxide, titanium oxide, zirconium oxide, tantalum oxide, niobium oxide, and selenium oxide; or

a gas barrier low moisture permeable insulating transparent substrate for an electrode, wherein a transparent macromolecule layer is laminated on a transparent substrate and/or on a transparent thin film; or

a gas barrier low moisture permeable insulating transparent substrate for an electrode, wherein a transparent macromolecule layer is laminated on a transparent thin film of a transparent substrate for an electrode, further a transparent thin film, a transparent substrate are successively laminated; or

a gas barrier low moisture permeable insulating transparent substrate for an electrode, wherein a hardening resin and/or the thermoplastic resin is laminated on at least one of the surface of a transparent substrate for an electrode; or

a gas barrier low moisture permeable insulating transparent substrate for an electrode, wherein a transparent macromolecule layer consists of at least one sort in a gas-permeability-proof resin, an anchor-coat agent, a hardening resin, and thermoplastic resin; or

a gas barrier low moisture permeable insulating transparent substrate for an electrode, wherein a gas-permeability-proof resin is the polymer or the mixture containing at least one component at more than 60 mol % of cellulose component, polyamide system resinous principle, vinyl alcohol component, halogenation vinylidene component, acrylonitrile component, and amorphous polyester component; or

a gas barrier low moisture permeable insulating transparent substrate for an electrode, wherein an anchor-coat agent consists of at least one sort of polyurethane, polyamide, polyethyleneimine, amorphous polyester, hydrophilic-property polyester, ion macromolecule complex, and alkyl titanate resin, those copolymers, or mixture; or

a gas barrier low moisture permeable insulating transparent substrate for an electrode, wherein a hardening resin consists of at least one sort of urethane resin, epoxy

resin, acrylic resin, acrylic-ester resin, phenoxy ether system, melamine resin, phenol resin, silicone resin, xylene resin, guanamine resin, diallyl phthalate resin, vinyl ester resin, polyimide, maleic resin, unsaturated polyester resin, and alkyd resin, those copolymers, or mixture; or

a gas barrier low moisture permeable insulating transparent substrate for an electrode, wherein a thermoplastic resin consists of at least one sort of polypropylene, polyethylene, polyolefines such as ethylene propylene copolymer, polyester, polyamide, ionomer, ethylene-vinyl acetate copolymer, acrylic ester, acrylic resin such as methacrylic-acid ester, poly-vinyl acetal, phenol, denaturation epoxy resin, vinyl acetate resin, silicone RTV, polymer alloy type polyimides, these copolymers, or mixture; or

a gas barrier low moisture permeable transparent conductive electrode substrate characterized by forming a transparent conductive thin film on the at least one of the gas barrier low moisture permeable insulating transparent substrate for an electrode.

[0014] Namely, this invention is made to solve the above-mentioned problem and comprises as a desirable mode:

a gas barrier low moisture permeable insulating transparent substrate for an electrode formed by laminating at least one of nitride layer and oxide layer respectively;

as more desirable mode, a gas barrier low moisture permeable insulating transparent substrate for an electrode formed by laminating at least one of multilayer transparent thin film layer that consists of nitride layer / oxide layer / nitride layer, or oxide layer / nitride layer / oxide layer etc. on one side or both sides of a transparent high polymer film base material suitably; further

a gas barrier low moisture permeable insulating transparent substrate for an electrode applicable to a liquid crystal display element, an EL element, etc., wherein a transparent macromolecule layer is laminated on at least one side of said transparent substrate for an electrode or between a transparent thin film and a high polymer film, especially the transparent macromolecule layer is a barrier transparent electrode film that contains a permeability-proof layer which consists of polymer which contains at least one component of vinyl alcohol, vinylidene chloride, or acrylonitrile at more than 60% or copolymer containing these components.

[0015] It is not limited to these examples that transparent substrates are films, such as polyester, polycarbonate, polysulfone, polyether sulphone, polymethylmethacrylate, polyvinyl chloride, cellulose, polyacetate, polly 4-methyl pentene -1, polyacrylonitrile system resin, phenoxy resin, polyphenylene-oxide system resin, poly-parabanic acid, and polystyrene, and should just be films which have low-leveled as it is transparent.

[0016] However, in the case of using for liquid crystal displays, from the viewpoint of PET of a uniaxial stretching or the optical isotropy, amorphous films, such as PES, polyarylate and polycarbonate, are desirable. And 30nm or less of the retardation

value of a usable film is 15nm or less preferably.

[0017] As a technique of producing such a film, it can be adapted in the conventional method of the extrusion method, the casting method and the rolling-out method. The thickness of a film is in the range of 10 to 1,000 μm usually, 20 to 400 nm preferably, 50 to 300 nm more preferably.

[0018] As desirable nitride as a material that constitutes a transparent thin film, silicon nitride, tin nitride, aluminum nitride, indium nitride, gallium nitride, boron nitride, chromium nitride, etc. are illustrated. As the light transmission, anything is sufficient as long as it is 50% or more usually, 70% or more preferably, 80% or more still preferably. In this case, a part of nitride may be oxidized or hydrogenated.

[0019] As what a part of nitride is oxidized as a material that constitutes a transparent thin film, acid nitrides, such as acid aluminum nitride, acid indium nitride, acid gallium nitride, acid silicon nitride, acid tin nitride, acid boron nitride, acid chromium nitride and acid silicon nitride carbide, are mentioned, for example. The nitrogen content in the component except the metal of these acid nitrides is more than 50 atom % still preferably more than 30 atom %.

[0020] As what a part of nitride is hydrogenated as a material that constitutes a transparent thin film, hydrogenation nitrides, such as hydrogenation aluminum nitride, hydrogenation indium nitride, hydrogenation gallium nitride, hydrogenation silicon nitride, hydrogenation tin nitride, hydrogenation boron nitride, hydrogenation chromium nitride and hydrogenation silicon nitride carbide, are mentioned, for example. The nitrogen content in the component except the metal of these hydrogenation nitrides is more than 80 atom % still preferably more than 50 atom %.

[0021] As mentioned above, a transparent thin film which consists of nitride consists of the monolayer field or the layered product of a transparent thin film comprising at least one kind of nitrides, acid nitride and hydrogenation nitride. The thickness of a transparent thin film which consists of this nitride is 0.3 nm to 500 nm usually, 1 nm to 100 nm preferably, 10 nm to 30 nm more preferably, and 5 nm to 50 nm still preferably.

[0022] As desirable oxide as a material that constitutes a transparent thin film, although the monolayer field or the layered product of the oxides which consist of at least one kind of oxides, such as indium oxide, indium oxide · tin (ITO), tin oxide, zinc oxide, aluminum oxide, silicon oxide, titanium oxide, zirconium oxide, tantalum oxide, niobium oxide and selenium oxide, is illustrated. As the light transmission, anything is sufficient as long as it is 50% or more usually, 70% or more preferably, 80% or more still preferably. The thickness of a transparent thin film which consists of this oxide is 0.3 nm to 500 nm usually, 1 nm to 100 nm preferably, 10 nm to 30 nm more preferably, and 5 nm to 50 nm still preferably.

[0023] Since oxide or nitride makes polyvinyl alcohol system resin adhere firmly, these

laminated layers have the effect which raises air and steam barrier nature more. Furthermore, it is more desirable to prepare a transparent thin film on both sides if it has the same thickness. That is, it is more desirable to prepare a 200 nm layer on both sides rather than a 400nm layer on one side. If necessary, a different kind of nitride layers may be laminated as a nitride layer, or a different kind of oxide layers may be laminated as an oxide layer.

[0024] For example, in the case of using aluminum nitride that is weak for water or acid, the durability and an acid-proof layered product will be obtained if silicon oxide and silicon nitride with the durability and acid-proof is laminated.

[0025] As a concrete technique of forming a nitride layer or an oxide layer, technique, such as the vacuum deposition method, the ion-plating method, the sputtering method, the molecular-beam-epitaxy method (MBE), CVD, the MOCVD method and the plasma CVD method, are illustrated, and it can be chosen suitably according to the heat-resistant temperature of a transparent substrate etc. Moreover, in the case of preparing nitride by the reactant physical vapor deposition, any gas including nitrogen component such as nitrogen and ammonia is usable as nitrogen component supply. Moreover, in acid nitride and hydrogenation nitride, in addition to these nitrogen supply component, oxygen; hydrogen; what can supply oxygen component, for example, water; what can supply hydrogen component, for example, water; and methane; may be mixed to supply and may be supplied to the system separately. Needless to say, in the case of the non-reaction system, the aforementioned component donator may be introduced in the system to supply the component of a thin film.

[0026] As the hardening resin of a transparent macromolecule layer, at least one sort chosen out of the group which consists of urethane resin, epoxy resin, acrylic resin, acrylic-ester resin, phenoxy ether system bridge-formed resin, melamine resin, phenol resin, silicone resin, phenol resin, silicone resin, xylene resin, guanamine resin, diallyl phthalate resin, vinyl ester resin, polyimide, maleic resin, unsaturated polyester resin and alkyd resin, those copolymers, or those mixture, is desirable.

[0027] Furthermore, UV hardening resin, electron ray hardening resin and heat-hardening resin are illustrated. As UV hardening resin, epoxy acrylate, urethane acrylate, polyester acrylate, polyfunctional nature acrylate, polyether acrylate, silicon acrylate, polybutadiene acrylate, unsaturated polyester/styrene, polyene/thiol, poly-styryl methacrylate, UV hardening lacquer, and those copolymers and those mixture are used preferably.

[0028] As electron ray hardening resin, epoxy acrylate, urethane acrylate, polyester acrylate, polyfunctional nature acrylate, polyether acrylate, silicon acrylate, polybutadiene acrylate, unsaturated polyester/styrene, polyene/thiol, poly-styryl methacrylate, UV hardening lacquer, and those copolymers and those mixture are used

preferably.

[0029] As heat-hardening resin, epoxy resin, xylene resin, guanamine resin, diallyl phthalate resin, polyurethane, vinyl ester resin, unsaturated polyester, polyimide, melamine resin, maleic resin, urea resin, acrylic resin, silicone resin, alkyd resin, and those copolymers and those mixture are used preferably.

[0030] As thermoplastic resin of a transparent macromolecule layer, polypropylene, polyethylene, polyolefines such as ethylene propylene copolymer, polyester, polyamide, ionomer, polyvinyl acetate, ethylene-vinyl acetate copolymer, acrylic resins such as acrylic ester and methacrylic-acid ester, poly-vinyl acetal, phenol, denaturation epoxy resin, amorphous polyester, and those copolymers and those mixture are desirable. Needless to say, the mixture of heat-hardening resin and UV hardening resin can be used as hardening resin, or the mixture of xenotype resins can be used.

[0031] As gas-permeability-proof resin of a transparent macromolecule layer, polymer containing at least one component at more than 60 mol %, which is chosen out of acrylonitrile component, vinyl alcohol component, vinyl butyral component, cellulose system component, aramid component and halogenation vinylidene component, or those mixture is desirable.

[0032] As acrylonitrile component polymer, polyacrylonitrile, polyacrylonitrile-butadiene copolymer, etc. are raised. As vinyl alcohol component polymer, polyvinyl alcohol etc. is raised. As vinyl butyral component polymer, the mixture of polyvinyl butyral, polyvinyl butyral, epoxy resin etc. is raised.

[0033] As halogenation vinylidene component polymer, PVDC (polyvinylidene chloride), PVDC-VC copolymer, PVDC-acrylonitrile copolymer, PVDC-acrylic-ester copolymer or plural copolymers including several sorts of monomer that can be copolymerized with vinylidene chloride, PTFE, etc. are raised. Generally, since these gas-permeability-proof resins do not have a good adhesive property with a high polymer film, it may prepare an anchor coat at a transparent substrate before a gas-permeability-proof resin coat.

[0034] As anchor-coat agent of a transparent macromolecule layer, one sort which is chosen out of polyurethane, polyamide, polyethyleneimine, amorphous polyester, hydrophilic-property polyester, ion macromolecule complex, alkyl titanate resin, those copolymers, or mixture is desirable.

[0035] As a technique of coating gas-permeability-proof component, anchor coat, hardening component and thermoplastic component, usual techniques such as the air knife method, the gravi-coating method, the reverse-rolling method, the bar coat method and the spray method, are applicable. Moreover, a xeransis after coating and an aging processing can be performed by usual technique.

[0036] The thickness of these gas-permeability-proof resin layer, anchor-coat layer,

hardening resin layer and thermoplastic resin layer is about 0.5 to 200 μm usually, 1 to 50μm, 5 to 30μm more preferably.

[0037] As a transparent conductive layer, well-known 1) metals such as gold, silver, copper, aluminum and palladium and these alloys and the monolayer of metals and the layered product, 2) tin oxide, indium oxide, indium oxide·tin (ITO), zinc oxide, compound semiconductors of copper iodide etc., and the monolayer of those mixture, the laminating, 3) the layered films that combined the above 1) and 2), can be used conventionally.

[0038] As the concrete technique of forming a transparent conductive layer, techniques, such as the spray method, the metal spraying method, the metal plating method, the vacuum deposition method, the ion-plating method, the sputtering method, the molecular-beam-epitaxy method (MBE), the CVD method and the plasma CVD method, will be raised.

[0039] The thickness of a transparent conductive layer is 8 nm to 700 nm usually, 10 nm to 300 nm preferably, 50 nm to 150 nm more preferably.

[0040] Moreover, in forming a nitride layer, an oxide layer, a transparent conductive layer or a transparent macromolecule layer on a transparent substrate, you may give performing corona discharge processing, plasma treatment, glow discharge processing, reverse spatter processing, surface split-face-ized processing, chemical treatment, etc. and a well-known under coat as pretreatment of a substrate. Moreover, the aforementioned anchor-coat agent can also be used here for an under coat.

[0041] Moreover, although the gas barrier low moisture permeable insulating transparent substrate for an electrode of this invention has insulation, this insulation means that surface electrical resistance is more than 10,000 Ω/□. This insulation is attained by forming a nitride layer and an oxide layer by using nitride and oxide whose surface electrical resistance is more than 10,000 Ω/□, or forming a nitride layer and an oxide layer for conductive nitride and conductive oxide in superfluous nitrogen and/or oxygen, or forming a nitride layer and an oxide layer from a metal by supplying superfluous nitrogen and/or superfluous oxygen. If necessary, at the time of forming a film, the surface electrical resistance of each class and/or the layered product may be measured, and you may adjust the amount of supply of nitrogen and/or oxygen so that surface electrical resistance may become more than 10,000 Ω/□.

[0042] Here is denoted: the aforementioned transparent substrate (A); the aforementioned nitride (B); the aforementioned oxide (C); the transparent macromolecule layer (D); the anchor-coat agent (E); the hardening resin (F); the gas-permeability-proof resin (G); and the thermoplastic resin (H). A desirable example is as follows:

BCA, CBA, CBCA, BCBA, DBCA,

DCBA, DCBACB, CBDA, CBDAC, CBAD, CBADCB,
CBACB, ACBDA,
DCBCA, DCBCACBC, CBCDA, CBCDAC, CBCAD,
CBCADCBC, CBCACBC, ACBCDA,
DBCA, DBCABC, BCDA, BCDAC,
BCAD, BCADBC, BCABC, ABCDA,
DBCBA, DBCBABCB, BCBDA, BCBDAC, BCBAD,
ABCBDBCBA, FACBFGBCAF, FABCFGCBAF,
BAHCBFGF, FACBFBCA, FAHCBFGFBCHAF,
ABCBH, ABCFCBAH, ABCBGCBA, ACBCFCBCA,
ACBEGEBCA, FABCF, FABCGF.

Transparent substrates for electrodes laminated in the above order are raised. Here, it is contained the cases that B is the multilayer field of a different kind of nitride and C is the multilayer field of a different kind of oxide. Naturally, in the cases of laminating in other orders, other instantiations can be also used as long as the layered product film equips with transparency, dampproofing, gas barrier nature and insulation.

[0043] This invention comprises:

a gas barrier nature substrate containing a transparent thin film laminated at least one layer of nitride and oxide respectively;

a film for moisture proof for EL elements and an electrode substrate for liquid crystal display elements containing a transparent macromolecule layer on at least one side of this gas barrier nature substrate, the outside of this transparent thin film, or between this transparent thin film and this transparent substrate; and

a dampproofing and gas barrier nature insulating transparent electrode film containing a transparent macromolecule layer at least on one side of the transparent conductivity film, which is formed by laminating such a transparent conductive layer and this transparent thin film on a transparent high polymer film base material suitably, outside of this transparent thin film, between this transparent thin film and a transparent substrate, or under a transparent conductive layer.

[0044] Hereafter, this invention will be explained by using an example in detail.

[0045]

[Examples]

Example 1

A layered product of silicon nitride (20 nm in thickness) / indium oxide (20 nm in thickness) / silicon nitride (20 nm in thickness) is formed on one side of polyether sulfone (hereinafter referred to as PES) film with the retardation value of 5 nm and a thickness of 50 μm by the reactant DC magnetron spatter method. The surface electrical resistance of this layered product is more than 10,000 $\Omega/\square$. Next, on

silicon nitride of the aforementioned layered product, heat-hardening silicone resin (30 μm) is applied by the bar coat method, and then the PES film with a thickness of 100 μm is laminated thereon and it is held at 150 ℃ for twenty minutes, to form a dampproofing and gas barrier nature film. In measuring the oxygen transmittance of this film according to ASTM-D1434, it is 0.8 cc · m^{-2} · day^{-1}. Furthermore, in measuring the oxygen permeability in 100 % of relative humidity according to ASTM-D3985, it is less than 0.9 cc · m^{-2} · day^{-1}. Next, in measuring the moisture vapor transmission by ASTM-E96 (38 %C, 90 %RH), it is 0.2 g · m^{-2} · day^{-1}. A transparent electrode layer with 600 in thickness which consists of indium oxide · tin (ITO, In:Sn=9:1) is formed by the sputtering method on the transparent substrate of the aforementioned dampproofing and gas barrier nature film as a transparent electrode. The surface electrical resistance is 200 Ω/□, and the light transmission are 85 % (550 nm).

[0046]

Example 2

A layered product of silicon nitride (20 nm in thickness) / indium oxide (20 nm in thickness) / silicon nitride (20 nm in thickness) is formed on one side of PES film with the retardation value of 5 nm and a thickness of 100 μm by the reactant DC magnetron spatter method. The surface electrical resistance of this layered product is more than 10,000 Ω/□. Next, on silicon nitride of the aforementioned layered product, heat-hardening polyurethane is melted in the partially aromatic solvent of methyl ethyl ketone and cellosolve acetate (2:1) to laminate the heat-hardening polyurethane layer (10 nm in thickness) by the bar coat method, and polyvinyl alcohol is melted in water to laminate the polyvinyl alcohol layer (8 nm in thickness) by the bar coat method, serially. After melting heat-hardening silicone resin (20 μm in thickness) in toluene and applying by the bar coat method, it is held at 120 ℃ for five minutes, and then the PES film with a thickness of 100 μm is laminated thereon and it is held at 150 ℃ for twenty minutes, to form a dampproofing and gas barrier nature film. In measuring the oxygen transmittance of this film according to ASTM-D1434, it is 0.5 cc · m^{-2} · day^{-1}. Furthermore, in measuring the oxygen permeability in 100 % of relative humidity according to ASTM-D3985, it is less than 0.6 cc · m^{-2} · day^{-1}. Next, in measuring the moisture vapor transmission by ASTM-E96 (38 %C, 90 %RH), it is 0.2 g · m^{-2} · day^{-1}. A transparent electrode layer with 1000 in thickness which consists of indium oxide · tin (ITO, In:Sn=8:2) is formed by the sputtering method on the transparent substrate of the aforementioned dampproofing and gas barrier nature film as a transparent electrode. The surface electrical resistance is 60 Ω/□, and the light transmission are 80 % (550 nm).

[0047]

Example 3

A layered product of indium oxide (20 nm in thickness) / silicon nitride (20 nm in thickness) / indium oxide (20 nm in thickness) is formed on one side of PES film with a thickness of 100 μm by the reactant DC magnetron spatter method. The surface electrical resistance of this layered product is more than 10,000 Ω/□. Next, on indium oxide of the aforementioned layered product, heat-hardening silicone resin (30 μm in thickness) is melted in isopropyl alcohol to apply by the bar coat method and it is held at 100 ℃ for five minutes, and then the PES film with a thickness of 100 μm is laminated thereon by the dry-laminate method, and it is held at 140 ℃ for twenty minutes, to form a dampproofing and gas barrier nature film. In measuring the oxygen transmittance of this film according to ASTM-D1434, it is 0.9 $cc \cdot m^{-2} \cdot day^{-1}$. Furthermore, in measuring the oxygen permeability in 100 % of relative humidity according to ASTM-D3985, it is less than 1.0 $cc \cdot m^{-2} \cdot day^{-1}$. Next, in measuring the moisture vapor transmission by ASTM-E96 (38 %C, 90 %RH), it is 0.3 $g \cdot m^{-2} \cdot day^{-1}$.

[0048]

Example 4

A layered product of silicon nitride (40 nm in thickness) / indium oxide (40 nm in thickness) is formed on one side of polyarylate film with a thickness of 100 μm by the reactant DC magnetron spatter method. Next, on indium oxide of the aforementioned layered product, ethylene-vinyl acetate copolymer (15 μm in thickness) is laminated to apply heat-hardening silicone resin (30 μm in thickness) by the bar coat method and the polyarylate film with a thickness of 100 μm is laminated thereon, and then it is held at 150 ℃ for twenty minutes, to form a dampproofing and gas barrier nature film. In measuring the oxygen transmittance of this film according to ASTM-D1434, it is 0.5 $cc \cdot m^{-2} \cdot day^{-1}$. Furthermore, in measuring the oxygen permeability in 100 % of relative humidity according to ASTM-D3985, it is less than 0.5 $cc \cdot m^{-2} \cdot day^{-1}$. Next, in measuring the moisture vapor transmission by ASTM-E96 (38 %C, 90 %RH), it is 0.2 $g \cdot m^{-2} \cdot day^{-1}$.

[0049]

Example 5

A layered product of silicon nitride (40 nm in thickness) / indium oxide (40 nm in thickness) is formed on one side of PES film with a thickness of 100 μm by the reactant DC magnetron spatter method. The surface electrical resistance of this layered product is more than 10,000 Ω/□. Next, on indium oxide of the aforementioned layered product, heat-hardening silicone resin (30 μm in thickness) is melted in isopropyl alcohol to apply by the bar coat method and it is held at 100 ℃ for five minutes, and then the indium oxide side of the film with the same constrictor as the aforementioned layered product film is doubled with this silicone side and it is held at

150 ℃ for twenty minutes, to form a layered product of PES / silicon nitride / indium oxide / silicone / indium oxide / silicon nitride / PES and to form a dampproofing and gas barrier nature film. In measuring the oxygen transmittance of this film according to ASTM-D1434, it is 0.6 $cc \cdot m^{-2} \cdot day^{-1}$. Furthermore, in measuring the oxygen permeability in 100 % of relative humidity according to ASTM-D3985, it is less than 0.6 $cc \cdot m^{-2} \cdot day^{-1}$. Next, in measuring the moisture vapor transmission by ASTM-E96 (38 %C, 90 %RH), it is 0.1 $g \cdot m^{-2} \cdot day^{-1}$.

[0050]

Example 6

A layered product of indium oxide (10 nm in thickness) / silicon nitride (10 nm in thickness) / indium oxide (10 nm in thickness) is formed on one side of a polycarbonate film (PC) with a thickness of 100 μm by the reactant DC magnetron spatter method. The surface electrical resistance of this layered product is more than 10,000 Ω/□. Next, on indium oxide of the aforementioned layered product, heat-hardening silicone resin (30 μm in thickness) is melted in isopropyl alcohol to apply by the bar coat method and it is held at 100 ℃ for five minutes, and then the indium oxide side of the film with the same constrictor as the aforementioned layered product film is doubled with this silicone side and it is held at 140 ℃ for fifty minutes, to form a layered product of PC / indium oxide / silicon nitride / indium oxide / silicone resin / indium oxide / silicon nitride / indium oxide / PC and to form a dampproofing and gas barrier nature film. In measuring the oxygen transmittance of this film according to ASTM-D1434, it is 0.5 $cc \cdot m^{-2} \cdot day^{-1}$. Furthermore, in measuring the oxygen permeability in 100 % of relative humidity according to ASTM-D3985, it is less than 0.5 $cc \cdot m^{-2} \cdot day^{-1}$. Next, in measuring the moisture vapor transmission by ASTM-E96 (38 %C, 90 %RH), it is 0.1 $g \cdot m^{-2} \cdot day^{-1}$.

[0051]

Example 7

After laminating thermoplastic resin comprising polyester on the one side of the dampproofing and gas barrier nature film formed in Example 5 as a heat-sealing layer by extrusion coating to prepare a heat-sealing layer (50 μm in thickness), the two sheets are piled up so as to make the heat-sealing layers put each other inside, the electroluminescence field is inserted therebetween, and it is pasted up at 110 ℃ by a hot press to obtain an electroluminescence device. To these twenty pieces, the voltage of 400 Hz and 100 V is impressed to the cash-drawer electrode of each element, respectively, and the shunt test is performed. There is no poor shunt. Moreover, the remarkable fall of brightness do not occur after 100 hours at 60 ℃ and 90 %Rh.

[0052]

Example 8

On one side of PES with the retardation value of 5.0 nm and a thickness of 100 μm, in (a) the condensates with 70 deadweight % of adipic acid in 3 mols and trimethylol propane in 4.2 mols, and 30 deadweight % of ethyl acetate; and (b) the additional products with 75 deadweight % of tolylene diisocyanate in 3 mols and trimethylol propane, and 25 deadweight % of ethyl acetate, urethane resin which consists of the mixture of (a) 100 deadweight section and (b) 40 deadweight section is melted in methyl ethyl ketone (MEK) to apply by the bar coat method, and it is held at 150 ℃ for twenty five minutes after drying at 85 ℃ for five minutes to make it harden, and an under-coat layer with a thickness of 8 μm is prepared. Similarly, poly-vinyl alcoholic resin is melted in water to apply by the bar coat method and dry, and a poly-vinyl alcoholic layer with a thickness of 10μm is prepared. Next, a gas barrier film is obtained by laminating of silicon nitride (30 nm in thickness), silicon oxide (30 nm in thickness) and acid silicon nitride (30 nm in thickness) serially by the reactant RF ion-plating method on a poly-vinyl alcoholic layer. The surface electrical resistance of each class and this layered product is more than 10,000Ω/□. In measuring the oxygen transmittance of this film according to ASTM-D1434, it is 0.5 $cc \cdot m^{-2} \cdot day^{-1}$. Furthermore, in measuring the oxygen permeability in 100 % of relative humidity according to ASTM-D3985, it is less than 0.5 $cc \cdot m^{-2} \cdot day^{-1}$. Next, in measuring the moisture vapor transmission by ASTM-E96 (38 %C, 90 %RH), it is 0.1 $g \cdot m^{-2} \cdot day^{-1}$. A transparent electrode layer with 600 in thickness which consists of indium oxide·tin (ITO, In:Sn=9:1) is formed by the sputtering method on the transparent substrate of the aforementioned dampproofing and gas barrier nature film as a transparent electrode. The surface electrical resistance is 200 Ω/□, and the light transmission are 85 % (550 nm).

[0053]

Example 9

On one side of PES film with a thickness of 100 μm, a silicon nitride layer and an indium oxide layer are formed by the reactant DC magnetron spatter method, and a layered product of PET / silicon nitride (20 nm in thickness) / silicon oxide (20 nm in thickness) / indium oxide (20 nm in thickness) is formed by the reduced pressure plasma-chemistry gaseous-phase vacuum deposition (CVD) using tetramethyl disiloxane. The surface electrical resistance of this layered product is more than 10,000 Ω/□. Next, on indium oxide of the aforementioned layered product, heat-hardening silicone resin (30 μm in thickness) is melted in toluene to apply by the bar coat method and it is held at 120 ℃ for ten minutes, and further it is held at 140 ℃ for forty minutes to harden the heat-hardening silicone resin, and to form a dampproofing and gas barrier nature film. In measuring the oxygen transmittance of this film according to ASTM-D1434, it is 0.9 $cc \cdot m^{-2} \cdot day^{-1}$. Furthermore, in

measuring the oxygen permeability in 100 % of relative humidity according to ASTM-D3985, it is less than 1.0 cc·m^{-2}·day^{-1}. Next, in measuring the moisture vapor transmission by ASTM-E96 (38 %C, 90 %RH), it is 0.3 g·m^{-2}·day^{-1}.

[0054]

Comparative example 1

Regarding PET, PES and the polyarylate (PAR) with 100 μm, the following results are obtained from measuring the oxygen permeability in 100% of relative humidity according to ASTM-D3985 and the moisture vapor transmission according to ASTM-E96 (38 %C, 90 %RH).

[0055]

[Table 1]

	The light transmission %	The moisture vapor transmission g·m^{-2}·day^{-1}	The oxygen permeability cc·m^{-2}·day^{-1}
PET	86.3	7	11
PAR	88.1	50	30
PES	88	100	380

[0056]

Comparative example 2

A layered product of indium oxide (60 nm in thickness) is formed on one side of PES film with a thickness of 100 μm by the reactant DC magnetron spatter method. The surface electrical resistance of this layer is more than 10,000 Ω/□. Next, on indium oxide of the aforementioned layered product, heat-hardening silicone resin (30 μm in thickness) is melted in isopropyl alcohol to apply by the bar coat method and it is held at 100 ℃ for five minutes, a PES film with a thickness of 100 μm is laminated thereon and then it is held at 150 ℃ for twenty minutes, to form a layered product. In measuring the oxygen transmittance of this film according to ASTM-D1434, it is 20.2 cc·m^{-2}·day^{-1}. Furthermore, in measuring the oxygen permeability in 100 % of relative humidity according to ASTM-D3985, it is less than 30 cc·m^{-2}·day^{-1}. Next, in measuring the moisture vapor transmission by ASTM-E96 (38 %C, 90 %RH), it is 8 g·m^{-2}·day^{-1}.

[0057]

Comparative example 3

A polyvinyl alcohol layer (8 nm in thickness) is formed on one side of PES film with a thickness of 100 μm, and heat-hardening silicone resin (30 μm in thickness) is melted in isopropyl alcohol to apply by the bar coat method and it is held at 100 ℃ for five minutes, a PES film with a thickness of 100 μm is laminated thereon and then it is held at 150 ℃ for thirty minutes, to form a layered product. In measuring the oxygen transmittance of this film according to ASTM-D1434, it is 0.6

$cc \cdot m^{-2} \cdot day^{-1}$. Furthermore, in measuring the oxygen permeability in 100 % of relative humidity according to ASTM-D3985, it is less than 15 $cc \cdot m^{-2} \cdot day^{-1}$. Next, in measuring the moisture vapor transmission by ASTM-E96 (38 %C, 90 %RH), it is 20 $g \cdot m^{-2} \cdot day^{-1}$.

[0058]

Comparative example 4

A layered product of indium oxide (30 nm in thickness) is formed on one side of PES film with a thickness of 100 nm by the reactant DC magnetron spatter method. The surface electrical resistance of this layer is more than 10,000 Ω/□. Next, on indium oxide of the aforementioned layered product, heat-hardening silicone resin (30 μm in thickness) is melted in isopropyl alcohol to apply by the bar coat method and it is held at 100 ℃ for five minutes, and then the indium oxide side of the film with the same constrictor as the aforementioned layered product film is doubled with this silicone side and it is held at 120 ℃ for fifty minutes, to form a layered product of PC / indium oxide / silicone / indium oxide / PES and to form a dampproofing and gas barrier nature film. In measuring the oxygen transmittance of this film according to ASTM-D1434, it is 14 $cc \cdot m^{-2} \cdot day^{-1}$. Furthermore, in measuring the oxygen permeability in 100 % of relative humidity according to ASTM-D3985, it is less than 15 $cc \cdot m^{-2} \cdot day^{-1}$. Next, in measuring the moisture vapor transmission by ASTM-E96 (38 %C, 90 %RH), it is 5 $g \cdot m^{-2} \cdot day^{-1}$.

[0059]

Comparative example 5

A layered product of indium oxide (80 nm in thickness) is formed on one side of PES film with a thickness of 100 nm by the reactant DC magnetron spatter method. The surface electrical resistance of this layer is more than 10,000 Ω/□. Further, after laminating thermoplastic resin comprising polyester on the indium oxide as a heat-sealing layer by extrusion coating to prepare a heat-sealing layer (50 μm in thickness), the two sheets are piled up so as to make the heat-sealing layers put each other inside, the electroluminescence field is inserted therebetween, and it is pasted up at 110 ℃ by a hot press to obtain an electroluminescence device. To these twenty pieces, the voltage of 400 Hz and 100 V is impressed to the cash-drawer electrode of each element, respectively, and the shunt test is performed. Among twenty pieces, eleven pieces do not emit light by the shunt, or brightness falls remarkably. Moreover, the remarkable fall of brightness do not occur after 100 hours at 60 ℃ and 90 %Rh.

[0060]

[Effect of the Invention] Clearly from the above examples, it turns out that the substrate of this invention has the gas barrier nature, which is excellent in dampproofing and is extremely excellent in the broad humidity requirement. Therefore, according to this

invention, for example, a moisture-proof film which is excellent for EL elements, a gas barrier low moisture permeable insulating transparent substrate for an electrode which is excellent for liquid crystal displays and a gas barrier low moisture permeable transparent conductive electrode substrate formed by using them, can be obtained.

[Brief Description of the Drawings]

[Drawing 1] is an example of the lamination view of the transparent substrate for electrodes of this invention.

[Drawing 2] is an example of the lamination view of the transparent substrate for electrodes of this invention.

[Drawing 3] is an example of the lamination view of the dampproof film for EL elements, which is applied the transparent substrate for electrodes of this invention.

[Drawing 4] is an example of the cross section of the EL element, which is applied the transparent substrate for electrodes of this invention as a dampproof film.

[Description of Notations]

1	transparent substrate
2	nitride layer
3	oxide layer
4	transparent macromolecule layer
4a	anchor-coat layer
4b	gas-permeability-proof resin layer
4c	hardening resin layer
4d	thermoplastic resin layer
5	transparent conductive layer
6	gas barrier nature low moisture permeable transparent substrate for an electrode
7	light emitting layer
8	dielectric constant layer
9	drawer electrode (aluminum foil)